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54: Title of invention - Auxiliary agent composition for laundering

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Specification

1. Title of invention
Auxiliary agent composition for laundering

2. Claim
(1) An auxiliary agent composition, wherein a mixture consisting of (a) cationic surfactant and (b) cationic polymer and/or nonionic polymer is coated with copolymer containing
(A) at least one kind of basic monomer having the general formula (I),

(I)

(In the formula, R is hyfrogen or methyl group. R1 and R2 are alkyl group of C1 - C3. x is 1 - 4.),
(B) at least one kind of water insoluble or hardly water soluble monomer and
(C) at least one kind of water soluble monomer.

3. Detailed explanation of the invention.
Industrial application
The present invention refers to an auxiliary agent composition for laundering containing cationic surfactants. Especially, the present invention relates to an auxiliary agent composition for laundering which can be used together with a detergent containing anionic surfactant.

Conventional technology
In general, the laundering process utilizing the washer consists of water supply, washing, spining, laundering and spining. In order to promote the activity of auxiliary agents for laundering such as fabric

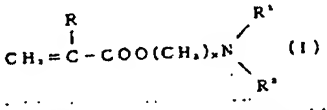
softener, finishing agent, etc., these agents have been added after completing the washing/laundering process. The conventional manual washer was operated step by step by a housewife, and under the said condition, addition of fabric softener, bleaching agent, starching agent, etc. to the laundering system after completing the main processes of laundering was not difficult. However, since use of semi-automatic or fully automatic washer has become popular, the housewive does no longer control the panel directly. However, the addition of the auxiliary agents into the said laundering system has not yet completely solved in the said automation system.
In order to include the auxiliary agent from the beginning of the laundering process, the active ingredient of the said agent should be protected during the washing stages. In other words, the auxiliary agent is adsorbed on the textile during laundering stages, and the active ingredient of the auxiliary agent should be released into rinsing water when the rinse cycle begins.

Problems to be solved by the invention

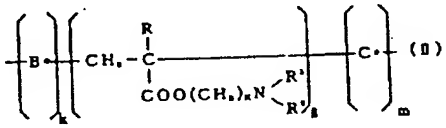
In case of coating the auxiliary agent for laundering with polymer which is substantially insoluble in alkaline detergent solution and is soluble in neutral rinsing solution, the active ingredient in the auxiliary agent is protected from from the alkaline washing solution during washing stage and can be released into the rinsing solution during the rinsing stage. In this case, the effect of the auxiliary agent can be used efficiently and furthermore, the process of adding the auxiliary agent during the laundering process can be eliminated since the auxiliary agent is added at the begining of the laundering process.
There are several different kinds of polymers which can show different solubility in the different pH ranges. For example, although polyvinylacetal diethylaminoacetate is insoluble in water at neutral range, the said compound is soluble when the pH of the system is lower than 5.8. On the other hand, although the copolymer of vinylpyrridine and acrylic acid is soluble in water when the pH is lower than 4 or is higher than 7.4, the compound is insoluble in water when the pH range is between 4 and 7.4. However, there have been no informations on the polymer which are insoluble in alkaline water, but is soluble in neutral and acidic water; in addition, the solubility of which can alter within a narrow range of pH. The present inventors have proposed the said copolymers and auxiliary agents coated with the said copolymers in Patent Journal Sho 58-247997.
However, in case of combining a fabric softener as the auxilary agent, the effectiveness is significantly reduced. As cationic surfactants such as quaternary ammonium salts are frequently used as the fabric softener, the anionic active agent remaining in the rinsing solution consumes the cationic surfactant. As aresult, the activity of auxiliary agent is reduced. In this case, it is necessary to add an excess amount of fabric softener.

Method of solving the said problems:

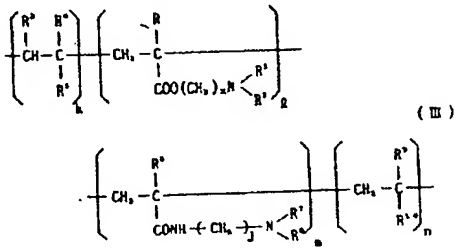
The purpose of the present invention is to provide an auxiliary agent of laundering which is protected safely in the alkaline washing solution during the washing stage and is released into the rinsing solution so that the activity of the auxiliary agent is expressed effectively.
In other words, the auxiliary agent consists of (a) cationic surfactant and (b) at least one kind of cationic polymer and/or nonionic polymer, and the said mixture is coated with a copolymer containing the following three monomers (A), (B) and (C).
(A) At least one kind of basic monomer having the following general formula (I),



(In the formula, R is hydrogen or methyl group. R1 and R2 are alkyl group of C1 - 3, respectively. x is 1 - 4.),
(B) At least one kind of water insoluble or hardly water soluble monomer, and
(C) at least one kind of water soluble monomers.
The said copolymer is substantially insoluble in alkaline water, and is soluble in neutral and acidic water. On the other hand, as the auxiliary agent for the laundering, it is necessary for the compound to be insoluble in an alkaline water of pH 9.5 or higher, and to be soluble in weakly alkaline to acidic water (less than pH 8.5). At the same time, the composition shows a high solubility under the presence of surfactants, preferably. Under the said point of view, the ratio of copolymer in (a) copolymer may be k/(k + l + m) = 0.05 - 0.8, l / (k + l + m) = 0.05 - 0.8 in the general formula (II), preferably k/ (K + l + m) = 0.05 - 0.6, l/ (k + l + m) = 0.1 - 0.7.



(In the formula, B· and C· are the composition units originated in the monomer (B) and the monomer (C), respectively.),
Furthermore, it is suitable that the degree of polymerization k + l + m is 100 - 50,000, preferably 300 - 20,000.
Preferable example of copolymer composition may be as follows:



R : H or $-CH_3$
R1 : alkyl group of C1 - C3
R2 : alkyl group of C1 - C3
x : 1 - 4
R3 : H or alkyl group of C1 - C4
R4 : H or alkyl group of C1 - C4, or $-COOR^{11}$ (R^{11} is alkyl group of C1 - C20)
R5 : $-COOR^{12}$, $-OCOR^{12}$ (R^{12} is alkyl group of C1 - C10?), $-C_5H_5$,
R6 : H or alkyl group of C1 - C4
R7 : R8 : may be same or different alkyl group of C1 - C4
J : 1 - 4
R9 : H or alkyl group of C1 - C4
R10: -OH, -CN, $-(CH_2)y\ OH$ (Whereas y = 1 - 4), $-CON\begin{matrix}R''\\R''\end{matrix}$

(R13 and R14 may be same or different , and are H or alkyl group of C1 - C18 ?),

$-COO(CH_2CH_2O)_pH$, $-COO(CH_2CH_2)_pCH_3$ (Whereas p = 1 - 30)

$k/(k+\ell+m+n) = 0.05 \sim 0.8$

$\ell/(k+\ell+m+n) = 0.05 \sim 0.8$

$m/(k+\ell+m+n) = 0.05 \sim 0.8$

$n/(k+\ell+m+n) = 0 \sim 0.5$

On the other hands, most preferable copolymer among the said copolymers described above can be indicated as follows: (In case of containing the 4th ingredient ($n \neq 0$) and in case of containing substantially no 4th ingredient).

(1) In case of containing the 4th ingredient;

R : H or $-CH_3$
R1 : $-CH_3$ or $-C_2H_5$
R2 : $-CH_3$ or $-C_2H_5$
R3 : H
R4 : H, $-CH_3$, $-COOR^{11}$ (R^{11} is alkyl group of C1 - C8 ?),
R5 : $-COOR^{12}$ (R^{12} is alkyl group of C1 - C8 ?) or $-OCOCH_3$,
R6 : H, $-CH_3$
R7 and R8 are $-CH_3$, $-C_2H_5$

J : 1 ~ 4

R' : H, $-CH_3$

R'' : $-COO(CH_2CH_2O)_pH$ (whereas p = 1 ~ 5),

$-COO(CH_2CH_2O)_pCH_3$ (whereas, p = 1 ~ 5), $-CON(CH_3)_2$,

$-CON(C_2H_5)_2$

$k/(k+\ell+m+n) = 0.05 \sim 0.5$.

$\ell/(k+\ell+m+n) = 0.1 \sim 0.65$.

$m/(k+\ell+m+n) = 0.1 \sim 0.6$.

$n/(k+\ell+m+n) = 0.01 \sim 0.5$

(2) In case of containing substantially the 4th ingredient;(n = 0)

R : H, $-CH_3$

R' : $-CH_3$, $-C_2H_5$

R'' : $-CH_3$, $-C_2H_5$

R^2 : H

R^4 : H, $-CH_3$, $-COOR''$ (R'' is alkyl group of C1 - C8 ?)

R5 : $-COOR^{12}$ (R^{12} is alkyl group of C1 - C8? (or C3?), or $-OCOCH_3$,

R^6 : H, $-CH_3$

R^7, R^8 : $-CH_3$, $-C_2H_5$

J : 1 ~ 4

$k/(k+\ell+m) = 0.05 \sim 0.6$.

$\ell/(k+\ell+m) = 0.1 \sim 0.7$.

$m/(k+\ell+m) = 0.1 \sim 0.7$

The practical examples of monomer ingredients (A), (B) and (C) are as follows:

Basic monomer (the 2nd ingredient of the general formula (III)) having the general formula (I)of (A) is one of the most important monomer ingredient capable of generating pH sensitive copolymer described in the present invention, and the practical examples of the said monomer ingredients are acrylic acid N,N-dimethylamino ethyl, acrylic acid N,N-dimethylaminomethyl, acrylic acid N,N-dimethylaminobutyl, acrylic acid N,N-dimethylaminopropyl, methacrylic acid N,N-dimethylaminoethyl, methacrylic acid N,N-dimethylaminomethyl, methacrylic acid N,N-dimethylaminobutyl, methacrylic acid N,N-dimethylaminopropyl, acrylic acid N,N-diethylaminoethyl, acrylic acid N,N-diethylaminomethyl, acrylic acid N,N-diethylaminobutyl, acrylic acid N,N,-diethylaminopropyl, methacrylic acid N,N-diethylaminoethyl, methacrylic acid N,N-diethylaminoethyl, methacrylic acid N,N-diethylaminobutyl, methacrylic acid N,N-diethylaminopropyl and so on. These compounds can be used singly or as a combination of more than two kinds.

Water insoluble or hardly water soluble monomer of (B) (the 1st ingredient of the general formula (III)) is the ingredient contributing the expansion of the water insoluble pH range of the pH sensitive copolymer. Practical examples of the said compounds are acrylic acid ester, methacrylic acid ester, crotonic acid ester, itaconic acid ester, vinylacetate and styrene. One or more than two kinds of the said compounds can be used in the present invention. In case of using alkyl ester of acrylic acid, methacrylic acid, crotonic acid and itaconic acid as

the monomer (B), the compound having alkyl group C1 - C18 (ester bond) can be used. However, when the alkyl chain length is too long, the rate of solubility of the copolymer in alkaline water becomes slow. Consequently, the chain length of the alkyl group may be 1 - 8. Preferable examples are acrylic acid ethyl, acrylic acid methyl, acrylic acid butyl, methacrylic acid methyl and methacrylic acid ethyl.
Water soluble monomer of (C) (the 3rd and 4th ingredients of the general formula (III)) contribites the expansion of the soluble pH range of the pH sensitive copolymer, and the practical examples of the said compounds are N,N-dimethylaminopropyl acrylic acid (or methacrylic acid) amide, N,N-dimethylaminomethylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminoethylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminobutylacrylic acid (or methacrylic acid) amide, 2-hydroxyethylacrylic acid (or methacrylic acid), 2-hydroxypropylacrylic acid (or methacrylic acid), polyethyleneglycol or methoxypolyethyleneglycol, (In both cases, an average adduct of ethylene glycol : p = 1 - 30), ester of acrylic acid or methacrylic acid. These compounds can be used singly or as a combination of more than two kinds.
The copolymers described in the present invention can be manufactured by the conventional radical polymerization reaction under normal pressure or positive pressure. The solvent systems used in the said polymerization may be acetone, etc., and the polymerization initiator may be azo-bis-isobutylonitrile, etc.
The polymerization temperature and the time may be different according to the type of polymerization solvent systems and combinations of various monomers. However, it is usually 40 - 90° C and 5 - 20 hours, respectively.
In the present invention, a mixture consisting of (a) cationic surfactant and (b) cationic polymer and/or nonionic polymer can be coated with the said copolymer.
Cationic surfactants used in the present invention are long chain dialkyl dimethyl ammonium salts, 1-methyl-1-long chain alkanoylaminoethyl-2-longchain alkylimidazolinium salt, and so on. Preferable salts of these compounds are chloride, methylsulfate, ethylsulfate and so on. These cationic surfactants are used as the fabric softener and fatty acid salts can be combined with the said surfactants. It is preferable to use powder or granular form of cationic surfactants (200 um or less in the diameter).
Cationic polymers are polydimethylaminoethyl methacrylate, dimethylamino ethyl methacrylate and acrylamide copolymer, polyacrylamide - cationic denatured polymer, etc. On the other hand, nonionic polymers are partially hydrolyzed products of polyacrylamide and polyacrylmide, and so on. The molecular weight of cationic polymer and nonionic polymer is preferably 500,000 - 10,000,000, most preferably 1,000,000 - 10,000,000. Furthermore, it is preferable to use powder or granular form of cationic polymer and nonionic polymer (200 um or less in the diameter).
The concentration of cationic polymer and nonionic polymer in the composition (100 weight parts of cationic surfactants) may be 1 - 50 weight

parts, preferably 2 - 10 weight parts.
The preparation of the mixture consisting of cationic surfactants and cationic polymer or nonionic polymer can be achieved by the conventional methods. The said mixture can be made into granule shape using the coating copolymer described in the present invention as the binder.
The method of manufacturing the auxiliary agent for laundering described in the present invention is as follows: 1 - 20 weight % of the coating copolymer is dissolved in organic solvent such as acetone, methanol, ethanol, etc., and granular form of the mixture consisting of cationic polymer or nonionic polymer and cationic surfactants which has been prepared separately is coated with the said coating polymer preparation using a pan or a fluid bed.
Another method is as follows: 30 - 60 weight % of the coating copolymer dissolved in organic solvent is mixed with cationic polymer or nonionic polymer and cationic surfactants, and a part of organic solvent is removed under reduced pressure; after pulverizing to a defined size of the granules, the organic solvent is completely removed under reduced pressure. Thus, the auxiliary agent for laundering coated with the copolymer can be prepared. The size of auxiliary agent for laundering prepared by the method described above is preparably 50 - 500 um, and furthermore, the amount of coating copolymer per the auxiliary agent composition is preferably 5 - 50 wt%.

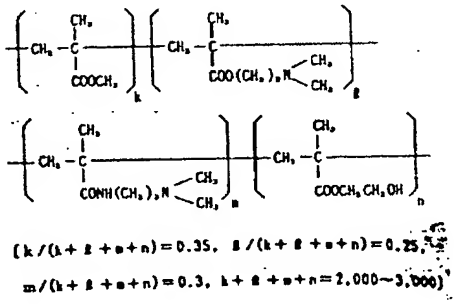
Function
According to the present invention, when cationic surfactant is coated with pH sensitive copolymer, the cationic surfactant is protected in the alkaline solution (laundering/ washing solution) and is releated into the rinsing water. In this case, the released agent is adsorbed on the textile and fabric softening activity and antistatic activity can be provided. In this case, cationic surfactant may be consumed by the action of anionic surfactants remaining in the rinsing solution. However, when cationic polymer and/or nonionic polymer exist in the said laundering system, the consumption of the cationic surfactant is inhibited effectively, and a desired fabric softening effect can be obtained.
As described above, the detergent composition described in the present invention can express a fine activity especially when the composition is added to the granular detergent containing anionic surfactants. It is convenient that the said composition may be added to the original composition of the detergent. It is also possible that the said composition can be prepared separately and the said composition and the detergent composition can be added simultaneously into the laundering system. Furthermore, the said composition can be used singly without combining with the detergent composition.

Effectiveness
According to the present invention, cationic surfactants in the washing solution are protected. When the composition is exposed to rinsing solution, the active ingredient is released into the rinsing solution.

Moreover, as the consumption of cationic surfactant by the residual anionic surfactant in the rinsing solution is inhibited in the present system, a small amount of the composition can generate the significant effectiveness.

Practical examples:

Practical example 1:
Forty-five weight parts of acetone solution containing 40 weight % of copolymer having the following chemical structure, 45 weight parts of powder (granule size 20 - 100 um in the diameter) distearyldimethyl ammonium chloride, 5 weight parts of powder silica and 5 weight parts of partially hydrolized product of polyacrylamide (the percent of partical hydrolysis : 5 %, molecular weight : 5,000,000, granular size : 20 - 100 um in the diameter) were mixed , and acetone was removed under reduced pressure. The mixture was then pulverized and granules of 35 - 150 mesh were prepared. The said granules were placed in a pan and acetone solution containing 5 weight % of the said copolymer was sprayed, and the total concentration of the copolymer used for coating the granules was 5 weight % as the solid. Thus, an auxiliary agent for laundering was prepared.



$(k/(k+\ell+o+n)=0.35,\ \ell/(k+\ell+o+n)=0.25,$

$m/(k+\ell+o+n)=0.3,\ k+\ell+o+n=2,000\sim3,000)$

Two g of the auxiliary agent composition for laundering prepared by the method described above and 40 g of commercial detergent composition (the heavy duty detergent composition containing linear alkylbenzene sulfonate - sodium salt as the major ingredient) were placed in a washer, and the test clothes (1 kg of cotton underwear, 0.3 kg of acryl shirt) were washed for 10 min, and after completing washing, the clothes were subjected for spin cycle. After removing excess water, the clothes were subjected for rinsing in 20 liter water twice for 3 min, and were dried in a room.

Practical example 2:
The test was carried out in the same manner as described in the practical example 1 except that partically hydrolyzed product of polyacrylamide was substituted with dimethylaminoethylmethylacrylate - acrylamide copolymer (degree of cationization : 30 mol %, molecular weight : 5,000,000 - 6,000,000, granular size : 20 - 100 um .).

Comparative example 1:
The test was carried out in the same manner as described in the practical example 1 except that a total amount of partically hydrolyzed product of polyacrylamide was replaced with powder silica.

Comparative example 2:
The test was carried out in the same manner as described in the practical example 1, except that the auxiliary agent composition for laundering was not employed. (The commercial detergent composition only was used.).
The softeness of the cotton towel treated with the test sample described above was evaluated by a panel consisting of 10 exparts (5 males and 5 females) by Scheffe's pair comparison method. The result is shown in Figure 1.

4. Simple explanation of Figure:
Figure 1 shows the diagram indicating the effect of the preparations prepared in the practical examples (softening effect of fabric softener).

No figure is shown in this text. ???